PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-012754

(43)Date of publication of application : 19.01.1999

(51)Int.Cl. C23C 20/04
B01J 13/00

(21)Application number : 09-180496

(22)Date of filing : 20.06.1997

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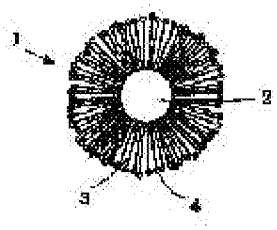
(54) PRODUCTION OF METALLIC THIN FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To make it possible to produce ultrathin films of metals under an atm. pressure by dropping a soln. contg. micell type particulates covering metallic particulates in a micellar form by adsorption of org. matter molecular chains on the surfaces of the metallic particulates onto a substrate and dissociating the cyrg. molecular chains after drying.

SOLUTION: While Cr, Zn, Te, Al, etc., are usable as the metallic particulates, multiple twin particles 2 of Au, Ag, Ni, Pd, Pt, Fe, Co, In, etc., are particularly used. The grain size thereof is preferably 1 to 200 nm. The molecular chains 3 of the org. matter are preferably mercaptoacetic acid, β-mercapltopropionic acid, alkanethiol, such as dodecanthiol, etc., and an alkyl group of 2-28C is more preferable. The soln. of the micell type metallic particulates 1 is applied on the substrate under the atm. pressure and after the soln. is removed by drying, the org. molecules bonded to the micell type metallic particulates 1 are subjected to heating, irradiation with UV rays, chemical treatment, etc., by which the metallic thin films having an arbitrary thickness are obtd.



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CLAIMS

[Claim(s)]
[Claim 1]A manufacturing method of a metal thin film by which dropping on a base a solution containing micell type metal particles which an organic matter chain stuck to the surface of metal particles, and covered metal particles in the shape of micell in a manufacturing method of a metal thin film, and being desorbed from an organic chain after desiccation.
[Claim 2]A manufacturing method of the metal thin film according to claim 1, wherein metal particles are multiplex twin crystal particles.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the method of manufacturing the super-thin film about one atomic layer thru/or a number atomic layer especially, about the method of producing a metaled super-thin film.
[0002]
[Description of the Prior Art]Thin films, such as metal, are used in various fields. Generally, by growing up the atom emitted to space by evaporation, sputtering, or other means, or a molecule on a base, the thin film is performed and for membrane formation of a thin film. It is made indispensable to carry out under a vacuum so that it may disperse without an obstacle from an evaporation source, and it is carried out under the high vacuum so that an adverse effect with a remains gas may not be received. For this reason, large-scale vacuum devices were indispensable to production of a thin film.
[0003]
[Problem(s) to be Solved by the Invention]This invention makes it a technical problem to provide the method of forming a thin film under atmospheric pressure, and makes it a technical problem to provide the method of manufacturing especially a metaled super-thin film.
[0004]
[Means for Solving the Problem]This invention is a manufacturing method of a metal thin film which trickles on a base a solution containing micell type metal particles which an organic matter chain stuck to the surface of metal particles, and covered metal particles in the shape of micell, and is desorbed from an organic chain after desiccation in a manufacturing method of a metal thin film.
[0005]Metal particles are the manufacturing methods of the aforementioned metal thin film which are multiplex twin crystal particles.
[0006]A metal thin film is a manufacturing method of the aforementioned metal thin film which is a metal super-thin film of one atomic layer - a number atomic layer.
[0007]
[Embodiment of the Invention]. this invention person etc. proposed this invention in Japanese

Patent Application No. No. 112066 [eight to]. The method of forming a metal thin film is provided by heat-treating it, after the solution containing the micell type metal particles which the chain of the organic matter stuck to the surface of metal particles, and covered metal particles to the micell type is dropped on a substrate. The micell type metal particles containing metal particles, Like the micell which the chain of the organic matter joined together, and the chain of the surface-active agent carried out the hydrophilic radical outside the center [a hydrophobic radical] in underwater exactly, and gathered in the surface of metal particles spherically, They are the micell type particles which the chain of many organic matters stuck to the metal particle surface chemically, and were spherically formed in it. And the obtained micell type particles show various kinds of characteristics based on the chemical nature of the chain of the organic matter which stuck to the surface of metal particles or metal particles.

[0008]For example, by changing the end of the chain of an organic matter into various kinds of things like a methyl group, a hydroxyl group, and a carboxyl group, character including the solubility over inorganic substances, such as various organic matters and water, etc. can be adjusted, or the substance which has various functions can be produced.

[0009]As shown in drawing 1, the chain 3 of the organic matter which has a surface of metal and compatibility on the surface of metal particles, especially the multiplex twin crystal particles 2 is sticking to the micell type metal particles 1 used for manufacture of the metal thin film of this invention, and micell type particles show the character based on the end functional group 4 of a chain.

[0010]Although various kinds of metal, such as chromium, ZnTe, selenium, aluminum, and copper, can be used as metal particles, multiplex twin crystal particles, such as gold, silver, nickel, palladium, platinum, iron, cobalt, and indium, are used especially. As for the particle diameter of metal particles, it is preferred that they are 1 nm - 200 nm, and it is more preferred that they are 10 nm - 100 nm. Since micell mold structure will not be formed if smaller than 1 nm, it is not desirable, and since it stops having the specific character as particles when larger than 200 nm, it is not desirable.

[0011]As a chain of an organic matter, alkane thiols, such as mercaptoacetic acid, beta-mercaptopropionic acid, and dodecanethiol, etc. are preferred, and the carbon number of an alkyl chain has a preferred thing of 2-18. It is linear shape, as for a chain, what seldom causes steric exclusion is good, and since obstacles, like a chain bends will be encountered if a carbon number becomes 20 or more, it is not preferred. More than 10^{-7}mol/l of the concentration of an organic matter is preferred, and an organic matter required if it becomes less than it, in order to form micell mold structure becomes less insufficient. as an end functional group of the chain of an organic matter, a hydroxyl group, a carboxyl group, a methyl group, a phenyl group, etc. are mentioned -- things can be carried out. The micell type particles dissolved to water can be prepared by using a hydrophilic radical as an end functional group. The substance etc. which have an adhesive property to metal, such as 4-META (4-metacryloxyethyl trimellitate anhydride), can be used.

[0012]Micell type particles are producible by mixing metal particles in the solution containing the chain of the organic matter made to stick to metal particles.

[0013]An example of the manufacturing process of the micell type metal particles used for this invention is explained with reference to drawing 2. Drawing 2 is a figure explained by a section. As shown in drawing 2 (A), into a vacuum, on the surface of the alkali halide crystals 5, such as salt, a metaled atom is vapor-deposited by a thickness of tens of nm, and the metal particles 6 are formed. As for the degree of vacuum in vacuum deposition, it is preferred that below 10^{-6}torr carries out. Subsequently, as shown in drawing 2 (B), the particles which vapor-deposited 100-200 nm of alkali halide, and produced it are thoroughly covered with alkali halide. As shown in drawing 2 (C), metal particles are further vapor-deposited on an alkali halide crystal face. By repeating the above process, as shown in drawing 2 (D), many metal particles 6 are producible. Metaled particles are not obtained, when the particles of the metal which adjoins in the case of metaled vacuum deposition unite and it becomes film-like metal. When metal arises in the shape of a film, it can check by the difference of a color from the metal of particle state. For example, in manufacturing golden particles by vacuum evaporation, it assumes a red purple color - blue by golden particles, but when gold foil arises, since it becomes golden, it can know that metal particles are not generating. Subsequently, the alkali halide which contained metaled particles as shown in drawing 2 (E), By dissolving into the solution 7 of the organic matter containing the chain to which it should stick, the chain of an organic matter sticks to the surface of the metal particles separated by the dissolution of alkali halide, and the micell type particles 1 of this invention as shown in drawing 2 (F) generate. Micell type particles can be separated from a solution and can be refined by the isolation column etc. which consist of polyimide etc. It is also possible to carry out separation refinement to residual substances, such as alkali halide and a thiol, by dialysis. It is meltable not only to alkali halide but a solvent, and a substrate is not combined with the metal used for metal particles, and if it forms with vacuum deposition, various kinds of substances can be used.

[0014]The solution containing the chain of the organic matter which sticks to the surface of metal particles, The solution of 10^{-3} - 10^{-6}mol/l has preferred concentration, when it is solution of mercaptoacetic acid and beta-mercaptopropionic acid, solution is preferred, and when it is a dodecane alkane thiol, the mixed liquor of ethanol and water is preferred. Since glycerin dissolves both alkali halide and an organic matter, when combining with the surface of metal particles the chain of the organic matter which does not dissolve in water, it can be used as a solvent.

[0015]In the bottom of atmospheric pressure with the manufacturing method of a metal thin film of this invention the solution of micell type metal particles, After it applies on a base and desiccation removes a solvent, the metal thin film of arbitrary thickness is producible by being desorbed from the organic molecule combined with micell type metal particles by heating, UV irradiation, a chemical treatment, etc. Although air may be sufficient as the formation atmosphere of a metal thin film, when metal reacts to atmosphere, it needs to use the atmosphere of the inert gas which does not react to the metal thin film to form.

[0016]It is also possible to form a metal thin film only in the arbitrary parts on a substrate. Drawing 3 is a figure explaining the formation process of a metal thin film. As shown in drawing

3 (A), the pattern of the adsorption region 9 which consists of an organic chain of micell type metal particles, such as photoresist, and an affinitive substance is formed in the field which forms a metal thin film on the substrate 8. Subsequently, when the solution of the thickness of the metal thin film which should be formed or the concentration according to a size, and the micell type metal particles of quantity is dropped or applied, micell type metal particles, It sticks to the affinitive adsorption region 9, and the substrate to which micell type metal particles adhered in the predetermined part as shown in drawing 3 (B) is obtained. Subsequently, if an organic molecule is desorbed after drying a solution, the metal thin film 10 patternized as shown in drawing 3 (C) will be obtained.

[0017]It is also possible to manufacture the metal super-thin film which has one atomic layer thru/or number atomic layer of a metal atom by the method of this invention. If the micell type metal particles which consist of particles of gold whose mean particle diameter is 7 nm are explained, the Kinbara child $1.2x10^{4}$ individual exists in this one particle. Therefore, since one drop is 0.01 ml when one drop of solution which prepared the micell type metal particles manufactured from golden particles to the concentration of $1x10^{-2}$mol/l is dropped at a silicon surface with an area of 1 square centimeter, The number of the micell type metal particles which exist in a silicon surface serves as $1x10^{-2}$mol/lx0.01-mlx Avogadro's number ($6.02x10^{23}$ individual / mol) $=6x10^{10}$. Therefore, the number of the Kinbara child who made it adhere to a silicon surface is a $6x10^{10}x1.2x10^{4}=7.2x10^{14}$ individual.

[0018]The number required for making gold of one atomic layer stick to a 1-square centimeter silicon surface is a $7.8x10^{14}$ individual, and is mostly in agreement with the above-mentioned value. Therefore, since the concentration of a metal particle aqueous micellar solution can produce the metal super-thin film of one atomic layer to the order of 10^{-2}mol/l, it also becomes possible to adjust the number of gold of one atomic layer, and to adsorb on a substrate. As mentioned above, according to the manufacturing method of the metal thin film of this invention, the metal thin film of predetermined thickness can be easily manufactured under atmospheric pressure from the metal thin film of one atomic layer.

[0019]

[Example]An example is given to below and this invention is explained to it.

Salt was vapor-deposited for the inside of example 1 vacuum devices in thickness of 100 nm on the 10 cm long and 10 cm wide substrate of ordinary temperature as a degree of vacuum of $2x10^{-6}$torr. Subsequently, the temperature of the substrate was heated at 300 **, the golden metal atom was vapor-deposited in thickness of 5 nm, and the particles whose particle diameter is an average of 7 nm were produced. Furthermore, the temperature of the substrate was held at 300 **, and salt was vapor-deposited in thickness of 100 nm. It carried out by having repeated the operation which vapor-deposits a golden metal atom in thickness of 5 nm, and vapor-deposits salt further on the formed salt, and the vacuum evaporation thing which contained in salt the metal particles which have ten layers of metal particle layers was obtained. The obtained vacuum evaporation thing was dissolved in the solution containing

beta-mercaptopropionic acid of concentration 10^{-3}mol/l, and the isolation column which consists of polyimide refined.

[0020]Subsequently, one drop was dropped at the surface of the silicon substrate {111} protected by the oxide film in the solution which prepared the concentration of micell type metal particles to the concentration of $1x10^{-2}$mol/l, and after drying, it measured in the reflection-high-energy-electron-diffraction device (RHEED). The picture acquired by measuring measurement on condition of incidence-electron-beams energy 15keV and an electron beam incidence direction <11-2> is shown in drawing 4 (A). The picture shows the pattern originating in gold of bulk state to the substrate face. Next, after heating a substrate for 0.5 second in 900 ** and cooling to a room temperature, the picture acquired by measuring in a reflection-high-energy-electron-diffraction device (RHEED) is shown in drawing 4 (B). the pattern peculiar to the state where one atomic layer of gold stuck to the silicon surface is shown, and the beta-mercaptopropionic acid which has covered the oxide film of a silicon surface and micell type gold particles ****s -- a silicon surface -- more than the carat of one atomic layer -- a thin film -- it was obtained and things have been checked.

[0021]

[Effect of the Invention]This invention by operation in which it is desorbed from the organic chain which forms micell after dropping or applying on a substrate the solution of micell type metal particles to which the chain which becomes the surface of metal particles from an organic matter was made to stick. The metal thin film of arbitrary thickness including a super-thin film [metal / of the thickness of one atomic layer] can be formed easily.

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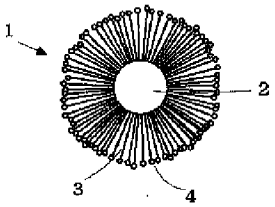
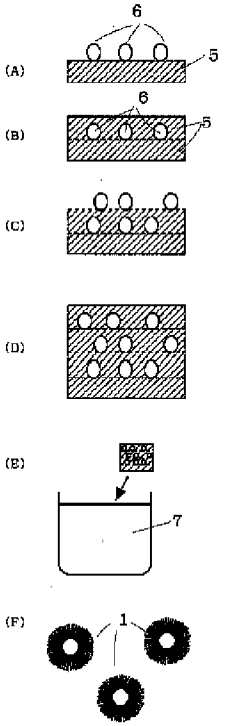
DRAWINGS

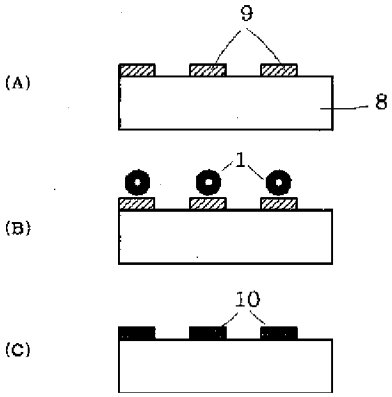
[Drawing 1]



[Drawing 2]



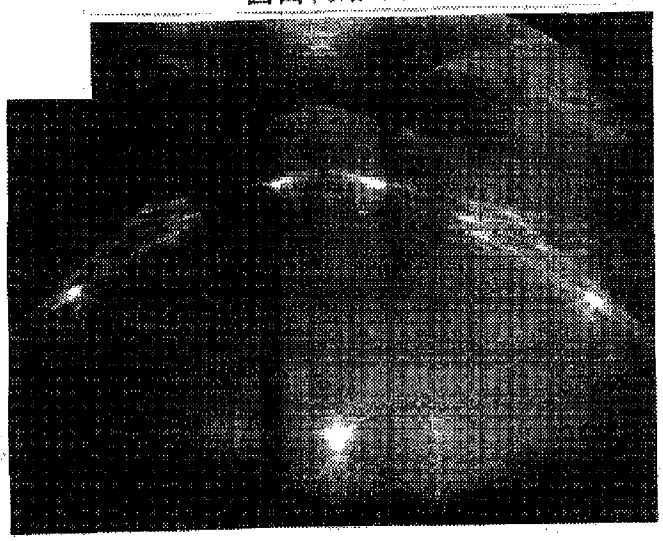
[Drawing 3]



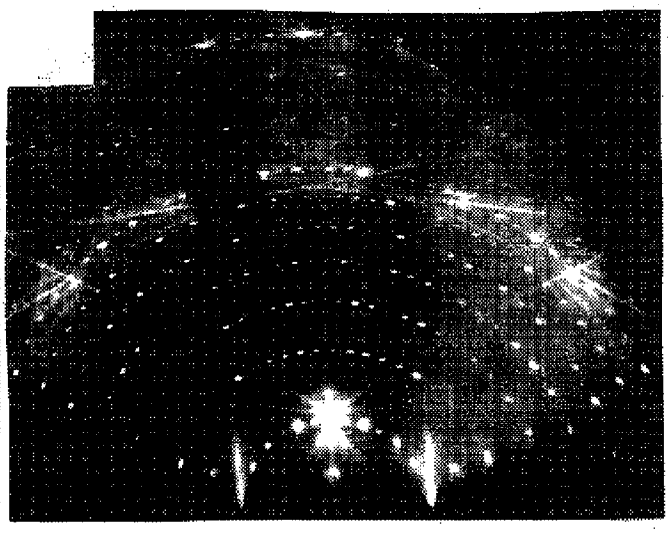
[Drawing 4]

図面代用写真

(A)



(B)



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